PHILOSOPHICAL MAGAZINE LETTERS, 2000, VOL. 80, NO. 3, 129–136

Plastic deformation of icosahedral Zn–Mg–Dy single quasicrystals

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[*Received in final form 8 November 1999 and accepted 22 November 1999*]

ABSTRACT

Plastic deformation experiments have been performed on Zn–Mg–Dy icosahedral single quasicrystals at temperatures between 490 and 530°C and at strain rates of 10^{-5} and $10^{-6}\,s^{-1}$. The stress–strain curves show strong yielding followed by a steady-state regime with a constant flow stress level up to strains of about 8%. Thermodynamic activation parameters of the deformation process were determined and are discussed in comparison with those found for icosahedral Al–Pd–Mn. Microstructural investigations by transmission electron microscopy on deformed samples were performed and indicate a deformation mechanism mediated by dislocations.

§ 1. INTRODUCTION

The mechanical properties of quasicrystalline materials have been the subject of several investigations in recent years. First experiments on single-grain icosahedral quasicrystals were performed on Al–Pd–Mn (Wollgarten *et al.* 1993), demonstrating that, despite the lack of translational symmetry in this class of materials, plasticity is mediated by a dislocation mechanism. The thermodynamic activation parameters of the deformation process for the same material were determined by Feuerbacher *et al.* (1995). Rosenfeld *et al.* (1995) carried out a detailed microstructural characterization of plastically deformed Al–Pd–Mn single quasicrystals. The conclusions of these studies were combined by Feuerbacher *et al.* (1997) into a qualitative model of the deformation process, namely the cluster friction model. In this model, the Mackay-type clusters, which are stable basic entities of the structure (Ebert *et al.* 1996, Janot 1996) act as rate-controlling obstacles to dislocation motion. In a later study, Messerschmidt *et al.* (1999) formulated a more quantitative model in terms of an extended Labusch–Schwartz theory, taking into account the high density and the extensions of the cluster obstacles.

In this letter, we present the first investigation of the plastic properties of single quasicrystals of icosahedral Zn–Mg–Dy. The family of stable quasicrystals in the

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Philosophical Magazine Letters ISSN 0950–0839 print/ISSN 1362–3036 online
http://www.tandf.co.uk/journals/tf/09500839.html

Zn–Mg–RE system (RE = rare-earth elements) was discovered by Luo *et al.* (1993). Systematic investigations of the phase diagram of Zn–Mg–Y by Langsdorf *et al.* (1997) served as a basis for attempts at single-quasicrystal growth. Large single grains of icosahedral Zn–Mg–RE were produced by Fisher *et al.* (1998) using the flux growth technique, by Langsdorf and Assmus (1998) using a liquid-encapsulated top-seeded solution growth technique and by Sato *et al.* (1998) using the Bridgman technique. The first plastic deformation experiments on icosahedral Zn–Mg–RE (RE= Y or Gd) were performed by Takeuchi *et al.* (1998) on coarse-grained material containing an unidentified second phase. The experiments described in the present study were performed on single-quasicrystal samples containing only the icosahedral phase. The results presented here can therefore be interpreted as the intrinsic plastic properties of this material.

§ 2. Experimental details

Icosahedral Zn–Mg–Dy quasicrystals were grown using the flux growth technique (Canfield and Fisk 1992, Fisher *et al.* 1998). The high-purity starting materials were sealed in a molybdenum crucible under vacuum conditions in the following proportions: zinc, 46 at.%; magnesium, 51 at.%; dysprosium, 3 at.%. The molybdenum crucible was sealed in a quartz tube in order to protect it against oxidation. The tube was placed in a chamber furnace on a water-cooled platinum tip, touching the bottom of the crucible and acting as a cold finger. With this local cooling, preferential grain nucleation at the centre of the crucible bottom was achieved. The furnace was heated to a temperature of 700°C, which is higher than the melting point of the alloy, in order to homogenize the melt. After 7 h a slow cooling sequence was started according to the following scheme: cooling to 650°C at 5°C h^{-1}, to 575°C at 1°C h^{-1} and to 480°C at 0.6°C h^{-1}. At 480°C the excess liquid was decanted. Following this procedure we were able to produce single quasicrystals of dodecahedral facetted morphology of up to 9 mm in diameter. The final composition of the single quasicrystals was determined as 62.8 at.% Zn–30.2 at.% Mg–7.0 at.% Dy by means of energy-dispersive X-ray analysis. The quality of the material was characterized by means of phase-contrast optical microscopy, scanning electron microscopy and transmission electron microscopy. We found that the material consists of a single phase, which was identified as the icosahedral phase of face-centred icosahedral structure, that is it possesses a face-centred hyperlattice. The electron diffraction patterns showed sharp spots properly aligned along the systematic rows, indicating a high structural perfection of the material.

For the deformation experiments rectangular samples of size about 3.2 mm × 1.3 mm × 1.3 mm were cut with a high-precision wire saw. The long axis, along the compression direction, was oriented parallel to a twofold direction. The surfaces were carefully ground and polished in order to prevent crack formation due to surface roughness. The plastic deformation tests were carried out in air at temperatures between 490 and 530°C. We used a Zwick Z050 testing machine under closed-loop control at constant strain rates of 10^{-6} and 10^{-5} s^{-1}. The length change was measured directly at the sample using a linear inductive differential transducer with an accuracy of 10 nm.

The activation volume V of the deformation process is determined according to

$$V = \frac{kT}{m_S I}, \tag{1}$$

where m_S is the Schmid factor, k is Boltzmann's constant, T is the absolute temperature and I is the strain-rate dependence of the flow stress. I can be obtained using the relation

$$I = \left.\frac{\partial \sigma}{\partial[\ln(\dot{\varepsilon})]}\right|_T = \left.\frac{\partial \sigma}{\partial[\ln(-\dot{\sigma})]}\right|_T. \tag{2}$$

The rightmost term in equation (2) allows the determination of I by means of a stress relaxation experiment, where the total strain is kept constant and the decrease in the stress is measured as a function of time. The middle term is used for the determination of I by strain-rate changes. Here the stress change resulting from an imposed sudden strain-rate change is measured.

The activation enthalpy ΔH was determined from combined stress relaxation experiments and temperature changes of 10°C according to the relation

$$\Delta H = -\frac{kT^2}{I}\left.\left(\frac{\partial \sigma}{\partial T}\right)\right|_{\dot{\varepsilon}}. \tag{3}$$

After deformation, the samples were rapidly unloaded and quenched in water within less than 30 s. They were cut into slices and prepared for transmission electron microscopy by subsequent grinding, polishing and argon ion milling on a liquid-nitrogen-cooled stage. The microstructural investigations were carried out using JEOL 2000EX and 4000FX transmission electron microscopes.

§ 3. Results

Figure 1 shows stress–strain curves for the icosahedral Zn–Mg–Dy single quasicrystals at a temperature of 500°C and strain rates of 10^{-5} and $10^{-6}\,\mathrm{s}^{-1}$. After having

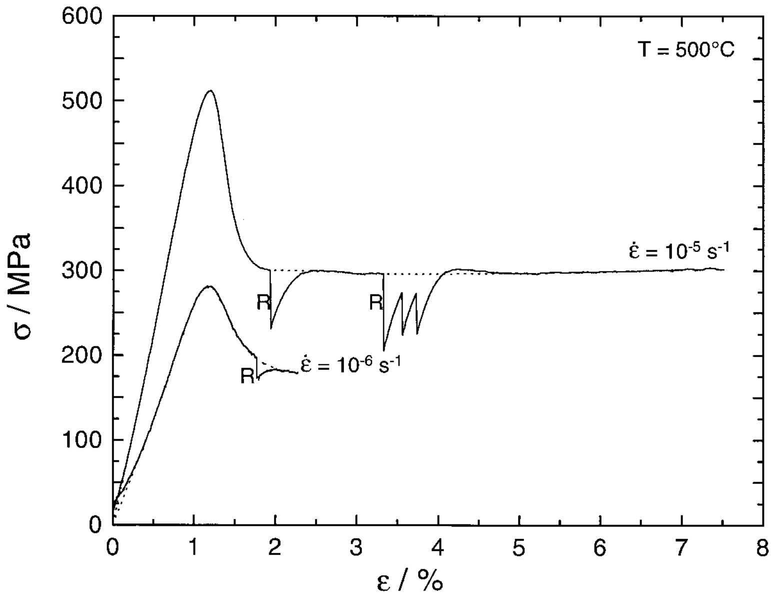

Figure 1. Stress–strain curves of icosahedral Zn–Mg–Dy at $T = 500$°C and strain rates of 10^{-5} and $10^{-6}\,\mathrm{s}^{-1}$. Vertical stress drops labelled R in the curves are imposed stress relaxation tests.

reached the upper yield point, both curves exhibit a pronounced yield drop down to about 60% of the upper yield stress. At $10^{-5}\,s^{-1}$ an upper yield stress of 510 MPa occurs at 1.2% strain, followed by a yield drop to 300 MPa. Then, up to 7.5% strain a steady-state range is found showing a constant flow stress level of 300 MPa. The curve corresponding to the deformation at $10^{-6}\,s^{-1}$ shows a lower upper yield stress of 280 MPa at 1.15% and a yield drop to 180 MPa at 2.2%. The vertical stress drops labelled R in the curves are imposed stress relaxation tests. The interpolated course of the stress–strain curves is shown in the figure as dotted lines.

Deformation tests at the lower temperatures of 400 and 450°C and a strain rate of $10^{-6}\,s^{-1}$ showed brittle behaviour, that is fracture of the specimens was found at negligible plastic strain. Successful deformation tests were carried out in the temperature range between 490 and 530°C at strain rates of 10^{-5} and $10^{-6}\,s^{-1}$. Figure 2 shows the upper yield stresses and the steady-state flow stresses determined. A monotonic decrease in the upper yield stress and the steady-state flow stress with increasing temperatures is found. Figure 3 shows a compilation of stress–strain curves at three different temperatures and a strain rate of $10^{-5}\,s^{-1}$. Stress relaxation tests, temperature changes and strain-rate changes are labelled R, TC and SRC respectively. All the curves have a number of features in common. They show a very pronounced yield drop and, after yielding, they reach a steady-state range, showing no further changes of the stress–strain behaviour up to the highest strains of our experiments. In the steady-state regime the curves show an almost constant flow stress.

The lowermost curve, obtained at 520°C, shows the typical course of a complete testing sequence. At a strain of 3% a stress relaxation was carried out, after which

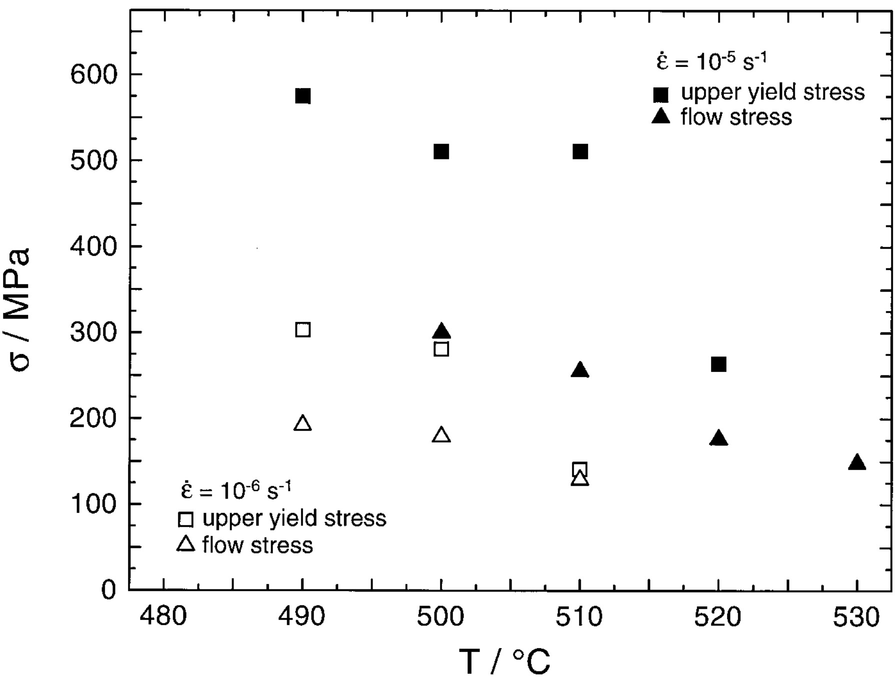

Figure 2. Upper yield stresses and steady-state flow stresses of icosahedral Zn–Mg–Dy at $\dot{\varepsilon} = 10^{-5}\,s^{-1}$ and $\dot{\varepsilon} = 10^{-6}\,s^{-1}$ for different deformation temperatures.

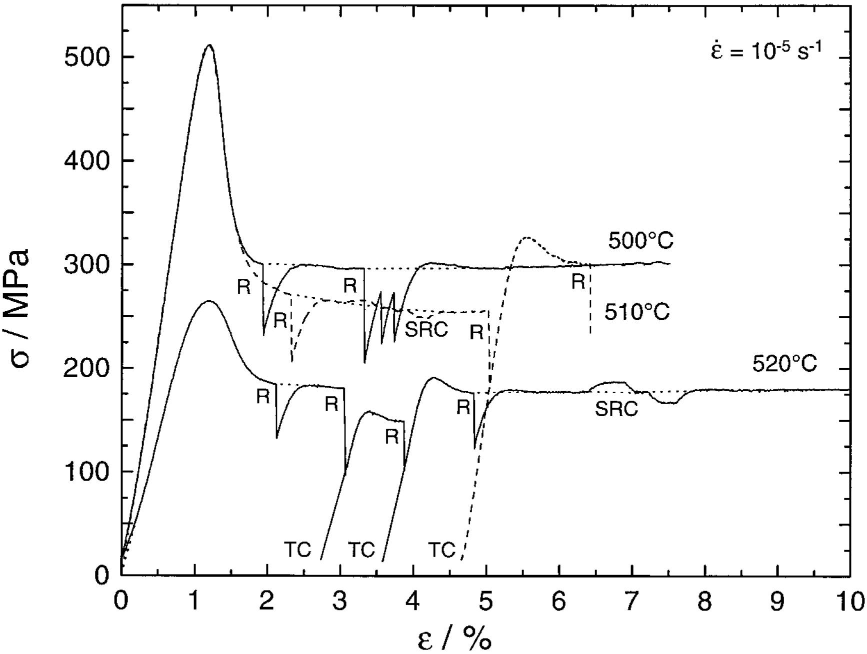

Figure 3. Stress–strain curves at different temperatures and a strain rate of $\dot{\varepsilon} = 10^{-5}\ s^{-1}$. Stress relaxation experiments (labelled R), strain-rate changes (labelled SRC) and temperature changes (labelled TC) were performed.

the sample was unloaded. The temperature was increased by 10°C and after an equilibration time of 30 min the sample was reloaded and the flow stress level at the second temperature was determined. Then the procedure was repeated, changing the temperature back to the initial temperature at which the rest of the curve was recorded. During the strain-rate change at about 7% the strain rate was subsequently changed to $1.2 \times 10^{-5}\ s^{-1}$, to $0.8 \times 10^{-5} s^{-1}$ and back to $1 \times 10^{-5} s^{-1}$. The resulting changes in the flow stress were determined. The uppermost curve of figure 3 (500°C) was previously shown in figure 1. The broken curve (510°C) shows a yielding behaviour which exactly corresponds to that at 500°C. In the course of this deformation test a strain-rate change (subsequently to $1.2 \times 10^{-5} s^{-1}$, to $0.8 \times 10^{-5} s^{-1}$ and back to $1 \times 10^{-5} s^{-1}$) at a strain of about 3.5% and a temperature change down to 500°C were performed. Note that the flow stress after the temperature change exactly corresponds to that of the curve recorded at 500°C.

We evaluated the activation volume from stress relaxation experiments (figure 4, full squares and circles) and strain-rate changes (figure 4, open squares) according to equations (1) and (2). The Schmid factor was chosen to be $m_S = 0.5$ because of the high isotropy of the icosahedral structure. We found activation volumes of between 0.61 nm^3 at 145 MPa and 0.28 nm^3 at 300 MPa. The data points evaluated from stress relaxation experiments at 10^{-5} and $10^{-6}\ s^{-1}$ and from strain-rate changes follow one universal curve. The activation volume shows a hyperbolic stress dependence (solid curve in figure 4). The stress exponent m was also determined by stress relaxation experiments. It slightly decreases from 3.6 at 490°C to 3.2 at 530°C.

The temperature changes of 10°C resulted in stress differences of 30 MPa at $T = 530$°C and 46 MPa at $T = 510$°C. The corresponding values of the activation

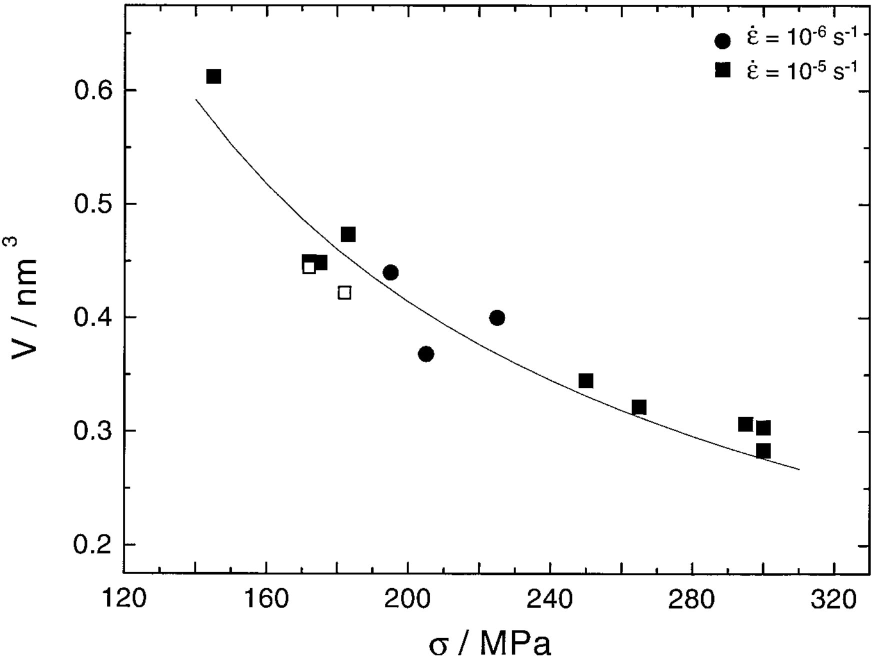

Figure 4. Activation volume evaluated from stress relaxation experiments at $\dot{\varepsilon} = 10^{-5}\,\mathrm{s}^{-1}$ (■) and $\dot{\varepsilon} = 10^{-6}\,\mathrm{s}^{-1}$ (●) and from strain-rate changes (□). Hyperbolic stress dependence (—).

enthalpy ΔH calculated according to equation (3) are 3.5 eV at 505°C and 3.9 eV at 525°C.

The deformed material was investigated by transmission electron microscopy under two-beam bright-field conditions. Samples deformed at a strain rate of $10^{-6}\,\mathrm{s}^{-1}$ at 500°C up to a plastic strain of 1.5% exhibit a dislocation density of $6 \times 10^9\,\mathrm{cm}^{-2}$. This is larger by three orders of magnitude than the dislocation density in the as-grown state, which was determined as $6 \times 10^6\,\mathrm{cm}^{-2}$. In addition, we found a large number of slip traces in deformed samples, which will be discussed in detail in a forthcoming paper (Heggen *et al.* 2000).

§ 4. Discussion

In this letter, the intrinsic plastic behaviour of icosahedral Zn–Mg–Dy quasicrystals is described for the first time. We performed macroscopic and microstructural investigations on single-phase single-quasicrystal samples in order to characterize the plastic deformation properties of this material. The observation of an increase in dislocation density by three orders of magnitude during plastic deformation gives direct evidence that the plastic deformation process is mediated by a dislocation mechanism. Close inspection of electron diffraction patterns of deformed material shows that no phase transition to a non-icosahedral structure takes place during deformation.

Plastic deformation of the specimens was possible at temperatures of 490°C and higher. At lower temperatures, fracture of the samples occurs. Therefore we can conclude that a brittle-to-ductile transition exists, located between 450 and 490°C for the range of strain rates applied in our experiments. At elevated temperatures, that is in the ductile regime, the stress–strain curves show an extraordinarily strong yield drop after the upper yield stress. Stress drops of about 40% of the maximum stress are observed, which is significantly more than for the case of icosahedral Al–Pd–Mn, yield drops of 10–15% of the maximum stress being found for that material (Schall *et al.* 1999).

At higher strains, after the yield drop, the stress–strain curves show an almost constant flow stress level, which we refer to as the steady-state flow stress. In this deformation stage, which extends up to the highest strains of about 8% in the present experiments, neither a significant hardening behaviour nor a significant softening behaviour is found. In this respect, the behaviour of icosahedral Zn–Mg–Dy differs from that of other quasicrystalline materials. All quasicrystalline materials on which deformation experiments have been performed to date show a softening behaviour at high strains, that is the flow stress continuously decreases with increasing strain. This has, for example, been observed for polycrystalline Al–Cu–Fe (Bresson and Gratias 1993) and for several other polycrystalline alloys (Kang and Dubois 1992), and also for single-quasicrystal Al–Pd–Mn (Wollgarten *et al.* 1993, Feuerbacher *et al.* 1997). On the other hand, for crystalline materials at higher strains an increase in the flow stress with increasing strain is observed in general and is referred to as work hardening. The present study shows that not a softening behaviour but rather a lack of work hardening should be regarded a characteristic feature of quasicrystal plastic deformation.

For a comparison of the steady-state flow stress with that of icosahedral Al–Pd–Mn, which is the most intensively studied quasicrystalline material as far as the plastic behaviour is concerned, we refer to the homologous temperature $T_{\mathrm{H}} = T/T_{\mathrm{m}}$, where T_{m} is the melting temperature of the material. According to differential temperature analysis, T_{m} is 600°C for our alloy composition, that is our experiments were conducted in the range from $T_{\mathrm{H}} = 87.4\%$ to $T_{\mathrm{H}} = 91.9\%$. At $T_{\mathrm{H}} = 88.5\%$ we observe a flow stress of 300 MPa. In icosahedral Al–Pd–Mn a flow stress of 320 MPa at $T_{\mathrm{H}} = 88\%$ was observed (Schall *et al.* 1999). Thus, the flow stresses of these alloys are very similar. However, at the same temperatures the upper yield stresses in Zn–Mg–Dy and Al–Pd–Mn are 510 and 400 MPa respectively. This large difference is due to the extraordinarily large yield drop effect in icosahedral Zn–Mg–Dy.

The activation volumes observed range from 0.61 to 0.28 nm^3, depending on the applied stress. The absolute values of the activation volume as well as its stress dependence are very close to the values found for icosahedral Al–Pd–Mn. This can be taken as an indication that the plastic deformation mechanisms of these alloys are similar. For icosahedral Al–Pd–Mn, a diffusion-controlled mechanism has been ruled out (Feuerbacher *et al.* 1995). The rate-controlling mechanism has been ascribed to the interaction of dislocations with elementary clusters (Feuerbacher *et al.* 1995). However, up to now, no structure model for icosahedral Zn–Mg–Dy has been established. Thus, for this material we cannot draw conclusions on the nature of the rate-controlling process in more detail.

The activation enthalpy of 3.5–3.9 eV is smaller than the values of about 6.5 and 5 eV at 750°C found by Feuerbacher *et al.* (1995) and Geyer *et al.* (2000) respectively. The values in the latter publication were corrected for recovery effects during the temperature changes. Taking into account the lower temperatures of our experiments and assuming a linear dependence of ΔH on the absolute temperature, the values found for icosahedral Zn–Mg–Dy correspond well to those found in the study of Geyer *et al.* (2000) for icosahedral Al–Pd–Mn.

Plastic deformation experiments on icosahedral Zn–Mg–RE (RE = Gd or Y) were conducted by Takeuchi *et al.* (1998) on coarse-grained material containing a second unknown phase. These experiments were performed between 150 and 400°C at a cross-head displacement of $3 \times 10^5 s^{-1}$, that is under experimental conditions where we could not achieve plastic deformation using our single-quasicrystal single-phase samples. Takeuchi *et al.* (1998) found an activation volume smaller than 1 nm^2 at high stresses, increasing to very large values of about 18 nm^2 as the stress approaches zero. They evaluated a total activation enthalpy of 1.9 eV. These values do not correspond well to our results. However, this is most probably due to the different experimental conditions and the different compositions and qualities of the samples.

Acknowledgements

We are grateful to C. Thomas and M. Beyss for their support with the quasicrystal growth. Ames Laboratory is operated for the US Department of Energy under contract W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

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